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MECHANISMS OF ACTIVATED CARBON DEGRADATION BY PERSPIRATION.(U)

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ED-CR-76066

MECHANISMS OF ACTIVATED CARBON  
DEGRADATION BY PERSPIRATION

Second Quarterly Progress Report  
October 1975 to December 1975

by

Dr. Louis L. Pytlewski

April 1976

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Amino acids harm the adsorption capacity of a carbon more than lactic or formic acid. Water can plug up carbon micropores. This water can be removed in a drying oven. In tests, the more harmful chemicals to adsorption capacity of an activated carbon were found to be synthetic sweat> glycine> glucosamine> d(-)-ribose> l-histidine> l-lysine> l-arginine> l-proline> di-citrulline> l-leucine> l-aspartic acid> glutamic acid> l-valine> l-serine> formic acid> dl-phenylalanine> KHCO <sub>3</sub> > uric acid> urea> NaCl> dl-alanine> CaCO <sub>3</sub> > lactic acid> H <sub>2</sub> O alone. The conduct of these tests is described.		

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Block 19

Lanolin

Bacterial effects

pH effects

Anion exchange system

Latex binders

Scotchgard

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# PREFACE

The work described in this report was authorized under Project/Task 1W762710A09506, Physical Protection Against Chemical Agents; Body Protection Investigations. This work was started in Oct. 1, 1975 and completed in Dec. 31, 1975.

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MECHANISMS OF ACTIVATED CARBON DEGRADATION  
BY PERSPIRATION

I. INTRODUCTION.

Activated carbon is a well known adsorbent for gases in an air sample. A layer of activated carbon granules is one of several layers in the construction of a protective garment for military personnel. Because of the nature of such a garment, it is heavy with airtight seals to the body, the wearer is subject to profuse sweating. Such sweating affects the activated carbon granules so that they rapidly lose their adsorptive capabilities.

Over the past three years we have been studying the ASC Whetlerite system under contract with the Pollution Abatement Division, Chemical Laboratory, Edgewood Arsenal, Dr. Joseph Epstein - Division Chief, with Dr. Leonard A. Jonas as immediate supervisor. We have built up quite a background on the physics and chemistry of plain and impregnated activated carbons relative to aging problems and toxic gas uptake mechanisms. Because of this expertise we have been asked by the Physical Protection Branch, Development and Engineering Directorate, to investigate the effects and possible cures for the adverse behavior of human sweat on activated carbon.

A great deal of precedental work has been done on this problem but as yet nothing useful has resulted. It is the consensus of opinion of past investigators that there is one component of sweat which is selectively, strongly adsorbed and "blocks off" the pores responsible for gas adsorption. Our early interaction with Mr. Thomas Mitchell (Textile Technologist, Dev. and Engineering Directorate) and a careful reading of the available published literature provided the following

(in synoptic form) helpful comments;

- A. There are basically two types of synthetic sweat formulations, one with and one without a substantial collection of amino acids. These are listed in the appendix at the end of the report. We have chosen to use the more complex form (formulation "a").
- B. Some investigators feel that lactic acid is the "culprit" - it does appear to reduce adsorptive effectiveness.
- C. The charcoal "binders" do not appear to cause or assist poisoning.
- D.  $\text{CCl}_4$  vapor has been the "model gas" in all previous studies. A  $\text{CCl}_4$  molecule has a  $7\text{\AA}$  effective diameter relative to surface coverage.
- E. Hydrophobic surface coatings on carbon at times appear to prevent poisoning - the use of Silanox 101 as a surface treatment has given erratic results. A good result here would indicate that water uptake is a significant contributor to poisoning.
- F. Regeneration of a good, adsorptive carbon is claimed by washing the garment in detergent.
- G. It is felt by some investigators that sebaceous oils should be added to synthetic sweat formulations.
- H. A chloropicrin "flow through" test would be a better indicator of effectiveness of carbons than the  $\text{CCl}_4$  (static) testing.
- I. When a plain, activated carbon is saturated with water, it loses ~75% of its adsorptive capability. This means that the loss in adsorptive capacity is proportional to the amount of substances in a carbon.



- J. Mathematical models of sweat on carbon are no help in solving the problem.
- K. An activated carbon is composed of micropores ( $<30\text{\AA}$  in diameter), a transitional pore dimension of  $>30\text{\AA}$  but less than  $2000\text{\AA}$ , and a macropore region of  $>2000\text{\AA}$  diameter. Micropore volume is about 80% of total internal volume.
- L. Radiation treatments of activated carbons were ineffective in preventing poisoning.
- M. All previous sweat studies did not take into account possible bacterial contributions and pH effects. A change in pH can allow for the production of volatile compounds from those of low volatility.
- N. Synthetic sweat formulations are odorless - real sweat certainly has volatile substituents.
- O. An undergarment has been made whose cellulosic component was chemically modified to give an anion exchange system which would allow for lactate ion uptake. An increase in breacktime is reported by the use of this garment. However, is this due to removal of "poisons" or simply the addition of another barrier to sweat diffusion to the activated carbon? We do feel that ion exchange could be a lucrative approach.
- P. Water insensitive latex binders reduce the effect of sweat poisoning.
- Q. "Scotchgard", a fluorochemical surface treatment which generates a hydrophobic and oleophobic surface on textiles has been reported to reduce sweat poisoning.
- R. Synthetic sweat formulations should also contain lanolin.

It should seem clear from the above statements that there is no, well-defined path already established and that our work will be "pioneer" in all directions that we choose to take. Our experimental approach will involve the following:

- A. Compound a synthetic sweat.
- B. Impregnate activated carbon with aqueous solutions of the components of the synthetic sweat and then measure  $\text{CCl}_4$  vapor uptake for each sample at several temperatures.
- C. Run synthetic sweat through a gas chromatograph using columns packed with activated carbon - both plain and impregnated types.  
It is hoped that this area will produce the most reliable information considering all aspects of the entire problem.
- D. Follow up part C (above) with real sweat.
- E. Investigate the influences of pH and bacterial attack on synthetic and real sweat using gas chromatography as the major source of pertinent information.
- F. Look at the use of hydrophobic/oleophobic and hydrophilic surface coatings on activated carbons.
- G. Conduct not just static measurements with  $\text{CCl}_4$  but also gas - "flow through" carbon bed tests in addition to looking at the effects of impregnants and surface coatings on activated carbons.
- H. Obtain adsorption isotherms for components which look promising as "poisons".

In this first phase of the sweat research it is our goal to answer the question as to the existence of "poison" either as a single source, or a conglomeration of sources such as acids.

## II. EXPERIMENTAL WORK.

Before any experimentation could begin, the components required for the synthetic sweat solution had to be purchased. The components and amounts used are shown in the appendix under Formulation "a".

Our gas chromatograph required a Flame Ionization Detector. This is now in place and we have been packing 1/8 in x 3 ft stainless steel columns with activated carbon and testing the physical parameters necessary to secure separation of various sweat samples into their components.

A Brunauer, Emmett, Teller (BET) apparatus to measure adsorption isotherms has been constructed and is now being calibrated.

Ten gram samples of activated carbon (15-30 mesh) have been treated by exposure to solutions of synthetic sweat and solutions of the components of sweat. In some cases the activated carbons were pretreated with pH buffers and hydrophobic silicone surface coatings. After the carbon was soaked in the solution of interest, it was oven dried to remove  $H_2O$ , then exposed to  $CCl_4$  vapor in a vacuum desiccator kept at a constant temperature of  $25^{\circ}C$ . The  $CCl_4$  weight uptake was determined and is reported here as  $\frac{\text{gms } CCl_4 \text{ adsorbed}}{\text{gm carbon}}$ . Data are shown in Table 1.

Table 1  
Effect of Synthetic Sweat and Synthetic Sweat  
Components\* on Carbon Tetrachloride Capacity  
of Plain Activated Carbon

Carbon Treatment	Capacity	Carbon Treatment	Capacity
	$\frac{\text{gm CCl}_4}{\text{gm C}}$		$\frac{\text{gm CCl}_4}{\text{gm C}}$
H <sub>2</sub> O alone	0.6787	l-Aspartic acid	0.2806
Lactic acid	0.4983	l-Leucine	0.2768
CaCO <sub>3</sub>	0.4803	dl-Citrulline	0.2720
dl-alanine	0.4724	l-proline	0.2390
NaCl	0.4691	l-arginine	0.2385
Urea	0.4446	l-Lysine	0.2244
Uric acid	0.4301	l-Histidine	0.2111
KHCO <sub>3</sub>	0.4267	d(-)Ribose	0.2068
dl-phenylalanine	0.4149	glucosamine	0.2007
Formic acid	0.4069	glycine	0.1976
l-Serine	0.4038	Syn. Sweat	0.1676
l-Valine	0.3012		
Glutamic acid	0.2931		

\* Synthetic sweat components are in concentration in H<sub>2</sub>O equal to that of the synthetic sweat



It should be noted that the effects of the treatments shown in Table 1 are listed in order of decrease in uptake of  $\text{CCl}_4$  vapor which can also be thought of as an increase in "poisoning" capability.

In an effort to overcome these poisoning effects, activated carbon was tumbled in a plastic breaker coated with dimethylpolysiloxane grease. This particular method produced a carbon which floats on water and yet has its pores open for adsorption. Carbon samples thus treated were subjected to solutions of synthetic sweat and to plain water.  $\text{CCl}_4$  uptake was measured. The results are shown in Table 2.

Table 2  
Effect of Silicone Treatment on Reducing Sweat  
Poisoning Effects

Carbon Treatment	Capacity
	$\frac{\text{gm CCl}_4}{\text{gm C}}$
Control - plain carbon, no treatment	0.5133
Carbon - silicone treated	0.5514
H <sub>2</sub> O alone	0.4116
Synthetic sweat solution	0.4719

As stated above, some carbons were pretreated with buffer solutions. One such solution consisted of a mixture of  $\text{K}_3\text{BO}_3$ ,  $\text{K}_2\text{CO}_3$ , and KOH at a pH of 10. After treatment,  $\text{CCl}_4$  capacity was measured. Results are shown in Table 3.



Table 3  
Effect of Carbon Pretreatment with pH 10  
Buffer on Reduction of Sweat Poisoning Effects

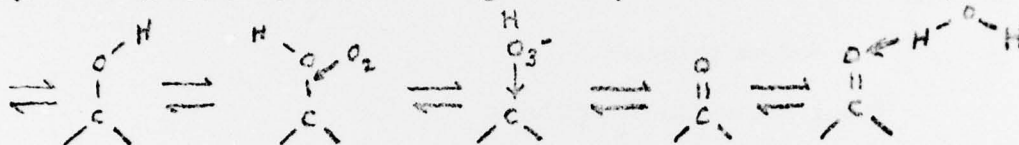
Carbon Treatment	Capacity
	$\frac{\text{gm CCl}_4}{\text{gm C}}$
Control-plain carbon, no treatment	0.5133
Carbon alone	0.4048
H <sub>2</sub> O alone	0.3351
Synthetic sweat solution	0.2956

### III. DISCUSSION.

It is clear from above that a hydrophobic coating on a carbon does enhance the adsorption of CCl<sub>4</sub> vapor in the presence of synthetic sweat. However, our data are still so sparse that it is unreasonable to say anything more definitive. If one wishes to survey the experiments in part II, there are some trends to be noted. The bulk of the amino acids used appear to do more damage to the adsorption capability of a carbon than certainly lactic acid and formic acid. In fact one can see a trend whereby the structural complexity of the molecular species is proportional to decrease in uptake of CCl<sub>4</sub>. Note also that the sugar types, glucosamine and d(-) ribose are close to the bottom of the list. Also, our cursory data indicate that lactic acid does the least damage alone of all the parts of our sweat solution. This is contrary to the expressions of earlier investigators.

An activated carbon depends upon its micropore structure for adsorption of gases. The micropore volume is roughly about 80% of the internal pores

volume. It is also important to keep in mind that an activated carbon must have a chemically active surface to be useful as an adsorbent. The loss in adsorptive capability can be due to the plugging of the micropores by large molecules and also the destruction of the active surface. Most experts feel that a carbon active surface contains a  $H_2O-O_2$ -carbon surface complex with an equilibrium distribution of a large variety of chemical bonds as;



Our investigations have shown that activated carbons carry a net negative surface charge and by this selectively pick up positively charged chemical species. An important conclusion from these works is that, in general, basic substances are more compatible with preservation of the activated carbon surface and acidic species tend to destroy surface activation. We can already faintly see some of these direction operating here.

Water alone can act to plug up the micropores although we have found that a  $H_2O$  saturated activated carbon can be made to lose rather readily about 95% of its adsorbed  $H_2O$  simply by heating in a drying oven. It has also been observed that an activated carbon allowed to soak in water at high ambient temperature for a period of weeks can lose its activation and thus lose completely its ability to adsorb gases and take on ASC Whetlerite impregnations.

#### IV. FUTURE WORK

During the last quarter of the contract period it is anticipated that we will have lots of good G.C. data. Furthermore, the previous experiments will be repeated for checks on reproducibility and also more carbon surface treatments will be examined. We will use activated carbons pre-impregnated with pH 1,3,5,7,9, buffers; impregnated with hydrophobic Tin hydrosols (as per PYTLEWSKI PATENTS); "Crown Ether" surface coatings; Fluorochemical-hydrophobic-oleophobic surface coatings.

# APPENDIX

## Formulation "a"

### Synthetic Sweat Formulations

- 1 - Spier, H.W. and Pascher, F. in Schuppi, R., ed.: Aktuelle Probleme der Dermatologie, V. 1, Karger, Basel, 1959, p.17.

Dissolve the following in 750 ml water, adjust to pH6 and dilute to one liter.

5 g sodium chloride

0.5 g potassium bicarbonate

0.5 g calcium carbonate

0.1 g lactic acid

0.01 g each: uric acid, formic acid, pyroglutamic acid, urconic acid, aspartic acid, glutamic acid, serine, alanine, proline, urea, glucose

0.005 g each: glycine, tyrosine, citrulline, valine, leucine, phenylalanine, tryptophan, histidine, ornithine, lysine, arginine, ribose, glycogen, glucosamine

## Formulation "b"

<u>COMPOUND</u>	<u>WEIGHT IN MILLIGRAMS</u>
Amino acid (41 mg. of dl Valine was used)	49.0
Ascorbic acid	4.0
Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	100.0
CaSO <sub>4</sub> · ½ H <sub>2</sub> O	50.0
Fe (SO <sub>4</sub> ) <sub>2</sub> (72% assay) (Ferric sulphate)	10.0
Glucose	207.0
Lactic acid	(low) 624.0 (high) 2095.0
MgSO <sub>4</sub> · 7H <sub>2</sub> O	20.0
Sodium chloride	5700.0
Urea	651.0
Uric acid	16.0
Distilled water	to make approximately 1000ml.

By adding concentrated ammonium hydroxide drop by drop by drop to adjust the pH, approximately 5-7 drops are required for adjustment to the low range, and approximately 10-14 drops are required for adjustment to the high range. The addition of ammonium hydroxide, besides adjusting the pH, serves to add the ammonia nitrogen that is required for the solutions. Although this addition of ammonium hydroxide does not add a specific amount of ammonia nitrogen, the amounts added do, however, fall within the range of ammonia nitrogen reported to be in human sweat.



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